Strontium concentration and isotopic ratio in CaCO3 matrix, marine carbonates and speleothems, by laser ablation MC-ICPMS

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We present a method to measure with a high precision both strontium isotopic ($^{87}Sr/^{86}Sr$) and Sr/Ca ratios in carbonate samples by Laser Ablation MC-ICPMS. The main interest in using laser ablation is to increase the spatial resolution of isotopic and Sr/Ca ratios and determine their relative variations along samples. To check strontium ratio accuracy during ablation measurements two carbonates with different isotopic signatures were used. One is the JCT (tridacna powder), a modern biocarbonate with a sea water signature at 0.70915. The other one is an in-house standard and corresponds to a Triassic coral with a strontium signature at 0.70770. To calibrate the ratio Sr/Ca we use the JCP standard (porites powder at 8.84 mmol/mol) and to check the accuracy of the strontium concentration, we use also the JCT standard (at 1.67 mmol/mol). We applied this method to a comparative exercise between analyses via solution and via laser ablation, on a well dated speleothem collected in an underground aqueduct from Paris, France. The Sr/Ca ratio shows a marked increase for the younger levels since the years 1850 while the $^{87}Sr/^{86}Sr$ isotopic composition falls from ca 0.70825 to ca 0.7080 in the same period. This can be connected with the increasing urbanization since the years 1850, with a waterproofing of the surface, and a longer residence time of the water within the underground system.